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ZERO-GRAVITY SOLIDIFICATION

FINAL REPORT

SPACE ENVIRONMENTAL EFFECTS ON SOLIDIFICATION STUDY

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Contract NAS8-21123

by

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FOREWORD

A summary report is presented on work performed during the period May to December 1969 on the Contract NAS8-21123, "Space Environmental Effects on Solidification." The reported work essentially fulfills the tasks stated in Modifications 4 and 6 to the original contract. These are:

- Define mechanism in solidification and phase change that may be perturbed by the environment of space, particularly zero-gravity
- Initiate a study to define materials having a high potential for production in space
- Define analytical models for study of the floating zone and Czochralski techniques for crystal growth
- Define major potential problem areas associated with solidification and crystal growth in spac
- Initiate theoretical and analytical studies to define the effects of the space environment, particularly zero-gravity, on the basic mechanisms involved in the solidification of materials having high potential for space processing including semiconductors, superconductors, ferroelectrics and other materials. Among the solidification techniques to be considered are unidirectional, solution transport, floating zone, and Czochralski. It is highly desirable to define analytically the functional dependence of impurity deposition and structural defects on solidification mechanisms in a zero-gravity environment.

This study program is sponsored by the George C. Marshall Space Flight Center, National Aeronautics and Space Administration, Huntsville, Alabama. Mr. T.C. Bannister is the director of the study. Dr. P.G. Grodzka, Research Specialist, Lockheed Missiles & Space Company, Huntsville Research & Engineering Center, Huntsville, Alabama, is the Principal Investigator.

SUMMARY

A theoretical analysis of the influence of various zero-gravity effects on solidification was conducted. Results of this analysis made possible the designation of five specific single crystals as candidates for manufacture in space orbit. The five candidates are silicon, germanium, KTN, BANANAS, and CuCl. Also, a number of considerations pertinent to space processing concepts and mathematical analysis theory are discussed.

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Section 1
INTRODUCTION

Lockheed's initial studies on the effects of the space environment on solidification were directed toward a thorough evaluation of the science and technology of thermal control of orbiting spacecraft by use of solid/liquid phase-change material (PCM). References 1 and 2 document the work performed in these studies.

While this work was in progress, the concept of utilizing the unique environment of space orbit for production purposes began to excite the imagination of a large segment of the scientific community. One of the most promising product areas foreseen for space production was that of single crystals and directly solidified composites for electronic and orbital applications. Knowledge and information generated on the subject contract was just the sort which was required for evaluating and innovating space processing concepts. Before full use can be made of the information, however, its relevancy to specific products and processing procedures must be analyzed. The work conducted for the nine-month period (May through December 1969) has been concerned mainly with such a relevancy analysis. Results of the present study include the identification and characterization of:

- Space environment effects on crystal growth and other solidification processes
- Products and materials having a high potential for space processing
- Processing concepts based on solidification most suitable for zero-g environments
- Potential problem areas associated with solidification in zero-g.

In addition, considerations pertinent to mathematically modeling floating-zone and the Czochralski techniques of crystal growth to include important zero-g effects are discussed. Although the mathematical modeling is restricted to the two cited techniques of crystal growth, the underlying considerations are equally applicable for modeling of general PCM behavior in zero-g environments.

Only materials and processing concepts which involved solidification from a liquid phase are considered. Crystal growth from vapor or solid phases is beyond the present scope.

Section 2

SPACE ENVIRONMENT EFFECTS ON CRYSTAL GROWTH AND ON OTHER SOLIDIFICATION PROCESSES

2.1 INTRODUCTION

In a previous report (Ref. 1), space environment effects on solidification processes are considered in detail. In the cited reference it is concluded that zero or near zero gravity fields will be the most important parameters affecting solidification behavior in space environments. Gravity affects solidification processes indirectly through buoyancy or convection. Convection determines the temperature and concentration fields in the fluid phase. Solidification processes, in turn, depend directly on temperature and concentration distributions. As a result of these considerations, three main advantages are foreseen for processes involving crystallization in near zero-g environments. These are:

- Elimination of gravity-driven convection
- Non-segregation of composites because of density differences
- Full use of surface tension forces in shaping, coating, and forming operations.

New or better products can be postulated which capitalize on each of these advantages. For example, the elimination of gravity-driven convection promises electronic and optical single crystals of unprecedented perfection. Ball bearings of hitherto unheard of tolerances possibly can be made by allowing metal melts to solidify while freely levitated under zero-g. A definite conclusion regarding the feasibility of such products, however, requires that a number of questions be considered further. Among these are:

- In what manner does convection influence crystal growth and thereby influence crystal perfection?
- What extent of convection is likely to be encountered under various g conditions?
- In what manner might non-gravity driving forces for mass movement be utilized for effecting new products?

These questions are considered in the following paragraphs although not in the order of their presentation. To answer the posed questions adequately, it is necessary to first consider the nature of melt and solution crystal growth, non-gravity driving forces for fluid flow, the scale of fluid motion, and coupling phenomena.

2.2 MELT AND SOLUTION GROWTH CHARACTERISTICS

In general, solution growth is not as desirable as is melt growth for high-quality single crystals. Solution growth is much slower and usually produces a relatively imperfect product. In certain circumstances, however, solution growth is the only practical means for growing an acceptable product. For this reason, it cannot be totally dismissed. A phase diagram, Fig. 1, for a simple eutectic will serve to illustrate the distinguishing characteristics of melt and solution growth.

Point A represents the melting point of pure S_1 and point E that of pure S_2. Melt growth of S_1 would occur well over on the left-hand portion of curve AC, while melt growth of S_2 well over on the right-hand side of curve EC. Regions of solution growth of S_1 and S_2 occur over the rest of the AC and EC curves. In the region of eutectic crystallization both S_1 and S_2 crystallize simultaneously. Obviously, when considering solution growth of any component, it is well not to get too close to the point of eutectic crystallization.

The dividing lines as shown in Fig. 1 were drawn rather arbitrarily. It remains for future studies to define precise criteria for the position of

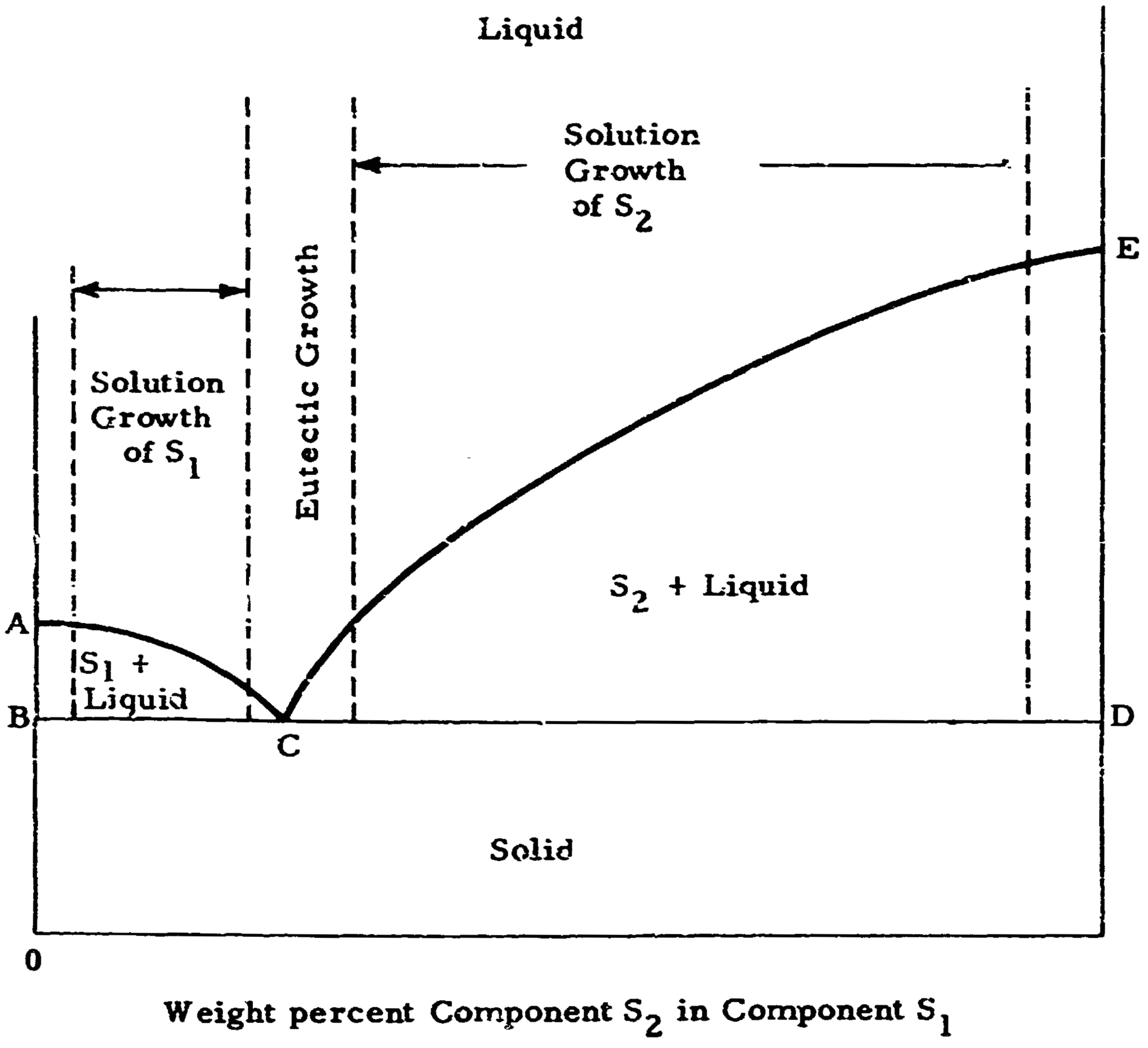


Fig. 1 - Schematic Phase Diagram for a Simple Eutectic System

the dividing lines. The point to be made here is that melt and solution crystal growth are not fundamentally different processes, but just a matter of degree of dominance of various possible rate processes. For example, in melt growth of S_1 because the amount of S_2 is very small, the rate of crystal growth will be determined either by the rate of heat transfer or the rate of the atomic attachment kinetics. In solution growth of S_1, because of the greater amount of S_2 component, the rate of diffusion of S_1 from solution to the crystallizing interface becomes important. One analysis of the relative importance of heat transfer and diffusion presents a simple criterion for determining which rate process is predominant (Ref. 3). This criterion is stated as follows:

$$\frac{1-c_r/c_\infty}{\ln(c_r/s)} = \frac{RT^2}{c_\infty DL}$$

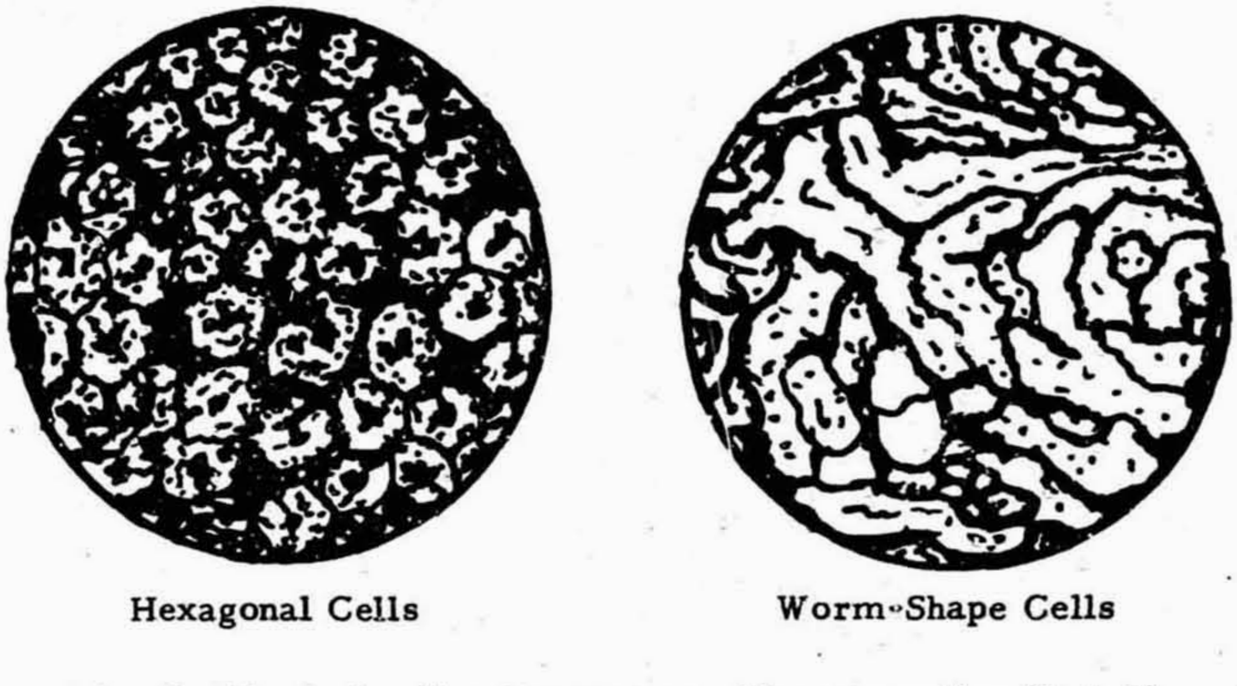
The term c_r is the concentration at the growing crystal interface, c_∞ the bulk concentration, s the crystal solubility, R the gas constant, T the temperature, D the diffusion coefficient and L the heat of solution. If either of the expressions is greater than one, $c_\infty > c_r \cong s$, and diffusion is the controlling rate. If either expression is much less than one, heat conduction is the limiting factor.

2.3 NON-GRAVITY DRIVEN CONVECTION

Liquid-vapor, liquid-liquid, and possibly liquid-solid interfacial tensions and also volume changes accompanying solidification are potential non-gravity forces for fluid flow. In the present study only the liquid-vapor and liquid-liquid interfacial tension driven flows are considered. Fluid flow caused by surface or interfacial tension gradients is called the Marangoni effect. (Several excellent general reviews of surface tension flows are given in Ref. 4). If a free liquid surface experiences a temperature or concentration gradient, a surface tension gradient will result because surface tension is a function of temperature and concentration.

Along the surface liquid will flow from the region of low surface tension to one of high surface tension. Usually, this will be from hot regions to colder regions because surface tension generally decreases with increase of temperature. The liquid moves faster near the surface, the depth of the disturbance depending on a variety of hydrodynamic parameters.

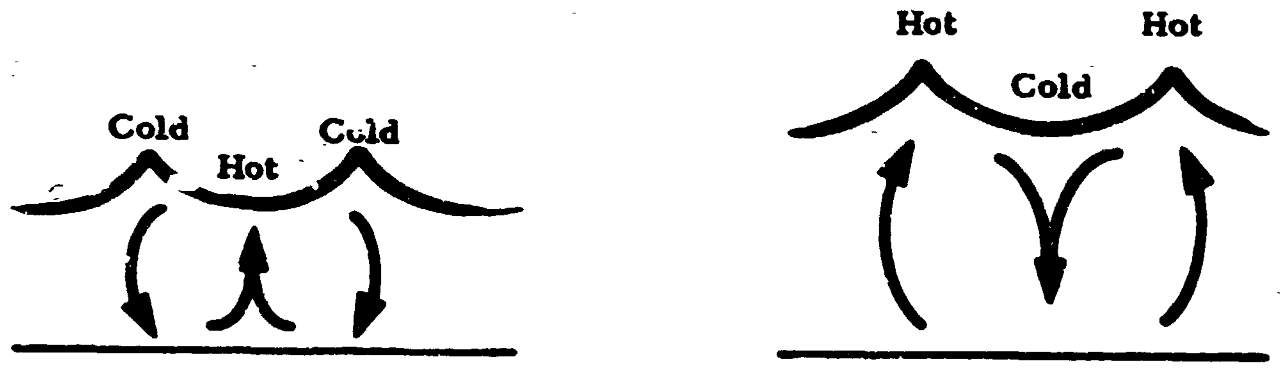
The occurrence of "tear drops" in a wine glass is a common illustration of the Marangoni effect. In this case evaporation of alcohol leaves the layer of liquid on the wetted glass wall with a higher surface tension than in the bulk of the liquid. As a result, liquid on the glass walls continuously draws up more liquid from the bulk until a "tear" is formed. When the "tear" becomes large enough, it falls back into the liquid. Another less commonly observed fluid motion also has its origin in surface tension gradient. A cellular motion results if a thin layer of fluid is heated from below and cooled from above. This type of convection flow was first investigated by Bénard in 1900. As viewed in perspective, Bénard cells present the appearance of a tray of doughnuts whose peripheries are squeezed together. Typical cell appearances, as viewed from above, are shown in Fig. 2.



Hexagonal Cells   Worm-Shape Cells

Fig. 2 - Typical cell patterns caused by convection (Ref. 5)

Lord Rayleigh developed a theory for cellular convection on the basis of an unstable density gradient. Rayleigh's theory, however, did not agree with all experimental observation. For example, cellular convection was found in shallow pools cooled from below; a stable situation according to Rayleigh's theory. Also the flow patterns observed in some instances were opposite to those predicted by Rayleigh's theory. Hot liquid was observed rising below centers of depression, whereas hot liquid would be expected to coincide with elevated regions if the flow were gravity driven (See Fig. 3). The discrepancies were resolved when both gravity and surface tension were recognized as possible motive forces for fluid flow. Couplings between surface tension and buoyancy were also recognized as a possibility.



Surface Tension-Driven Cells

Gravity-Driven Cells

Fig. 3 - Fluid Flow Patterns in Bénard and Rayleigh Convection Cells

In one analysis of cellular convection (Ref. 6), a stability criterion for surface tension-driven flows based on a dimensionless number B is given. This number, known as the Marangoni number, expresses the ratio of surface tension to viscous forces and is defined as

$$B = \frac{-\frac{d\gamma}{dT}\frac{dT}{dy}d^2}{\rho \nu \alpha}$$

where dT/dy, ν, α, ρ, and d are vertical temperature gradient, kinematic viscosity, thermal diffusivity, density and thickness of the fluid layer, respectively. The term dγ/dT represents the rate of change of surface tension with temperature.

For gravity-driven cellular convection the stability criterion is based on the Rayleigh number, which is given by

$$R = \frac{g\beta \frac{dT}{dy} d^4}{\nu\alpha}$$

where g is the acceleration due to gravity and β the coefficient of expansion.

2.4 MACROSCOPIC AND MICROSCOPIC CONVECTION CRITERIA

Whether a flow is classified as macroscopic or microscopic depends, of course, on the scale of interest. For example, gravity driven Bénard cells are considered in such large scale phenomena as cellular cloud patterns, polygonal distribution of rocks in certain arctic regions, and lunar craters (Ref. 7, p. 71). On the other hand, Bénard cells in sizes down to 50 microns are also commonly observed in thin fluid layers (Ref. 8). Both macroscopic and microscopic convection can influence the size and quality of single crystals, as discussed later. For the moment it is of interest to investigate what criterion might be used to decide which fluid flow driving force is predominant in any given situation. First of all it is necessary to define some measure of scale of motion. This requirement is conveniently fulfilled by a wavelength, λ. For example, the length of waves generated on a liquid surface by mechanical vibration, or the distance between two regions of repeating properties such as the distance between the cell walls of a Bénard cell.

In the case of waves on a liquid surface, their speed is given by the following formula if gravity is the dominant influence (Ref. 9)

$$c = \left[\frac{g\lambda}{2\pi}\right]^{1/2}$$

In the case where surface tension is the dominating force

$$c = \left[\frac{2\pi\gamma}{\lambda\rho}\right]^{1/2}$$

The following criteria, therefore, may be devised for deciding which force, gravity or surface tension, plays the predominant role (Ref. 10, pp. 597-598):

$$\frac{g}{\lambda} \gg \frac{4\pi^2\gamma}{\lambda^3\rho}$$ gravity-dominated waves

$$\frac{g}{\lambda} \ll \frac{4\pi^2\gamma}{\lambda^3\rho}$$ surface tension-dominated waves

2.5 COUPLING PHENOMENA

As previously stated, convection may affect crystal growth processes indirectly by altering the temperature and concentration field throughout the fluid phase. Because both convection and solidification mechanisms, however, depend directly on local temperature and concentration conditions, convection and solidification are seen to be dependent processes. In fact, they may be said to be coupled processes. Each is a response to imposed variations of a variety of possible independent parameters among which gravity must be numbered. The degree and manner of occurrence of either or both processes is thus interrelated. For example, the occurrence of compositional cells which have their origin in constitutional supercooling depends on the temperature gradient in the liquid phase (Ref. 11). The steeper the gradient, the less likely the occurrence of compositional cells. The steeper the external temperature gradient, however, the more likely that convection will result. The internal temperature gradient near the solid-liquid interface therefore may be reduced.

The presence of a moving solid-liquid interface which is liberating heat, in turn influences the convective field.

Systems under the influence of both gravity and surface tension forces may exhibit behavior unique to force couplings. For example, the speed of liquid surface waves is influenced by both gravity and surface tension. The coupling may be expressed in the following formula (Ref. 9):

$$c = \left[\frac{g\lambda}{2\pi} + \frac{2\pi\gamma}{\lambda\rho}\right]^{1/2}$$

For the case of cellular convection in thin fluid layers heated from below, the coupling is such that convection is predicted where none would be expected if the coupling were ignored. A criterion of instability when the coupling, under maximum reinforcement, between the two agencies is taken into account is given by Ref. 12.

$$\frac{R}{R_c} + \frac{B}{B_c} \geq 1$$

where R_c and B_c represent the critical values. In general, R and B reinforce each other in such a manner that cellular convection may occur at a Rayleigh number R and a Marangoni number B smaller than their corresponding critical values, R_c and B_c.

The phenomenon of convective overstability is still another area where coupling between gravity and surface tension appears to be an important fluid flow driving mechanism. When a fluid layer is subjected to an appropriate temperature gradient convection may set in as a stationary, cellular convection or as an oscillating convection with a characteristic frequency (Ref. 13). The flow can be pictured as proceeding in one direction for a time, coming to a halt, and then reversing (Ref. 14, p. 744). Overstable modes result in regular oscillations in temperature and are thus of considerable interest to crystal growers. Regular temperature oscillations have been observed in a number of cases in molten salts and in molten metals contained in horizontal boats across which temperature gradients are imposed (Refs. 15 and 16). Overstable oscillations have been the object of a large number of mathematical treatments. The outcomes of these treatments, however, have been somewhat inconsistent with actual observations. In particular, the presence of overstable convection was observed in cases prohibited by theory (Ref. 17). A recent treatment, (Ref. 17), however, establishes that the combined effects of buoyancy and surface tension gradients may lead to overstable oscillations in certain circumstances where oscillations, according to previous theory, would not be expected. The analysis presents criteria for stationary and overstable convective modes in terms of R, the Rayleigh number, R/B, the ratio of the Rayleigh number and B the Marangoni number, and a term representing a frequency characterization of the fluid velocity and temperature perturbation. Overstable oscillation is predicted for water heated from above between 0 and 4°C. Interestingly, observable melting and freezing oscillations are actually reported in one experimental study of freezing water in a temperature gradient (Ref. 18). No free liquid surfaces were present in the experimental study, thus raising the interesting possibility of liquid-solid interfacial tension involvement.

Mention of various less familiar types of convection is found in the literature. Among these are flows caused by liquid-liquid interfacial tension gradients. A cellular interfacial convection structure was found to accompany the extraction of acetic acid out of ethylene glycol with ethyl acetate (Ref. 19). The suggestion is forwarded that interfacial tension-driven flows may also be important at solid-liquid interfaces (Ref. 20). Thermosolutal convection results in certain situations. In this type of convection the solute concentration varies vertically in a gravity field. The result is a layering of convection regions. The origin for this type of convection lies in the differing rates at which heat and solute diffuse (Ref. 21).

2.6 CONVECTIVE EFFECTS ON CRYSTAL GROWTH

- Thermal Effects

Convection may affect crystal growth processes indirectly by altering the temperature and concentration field throughout the fluid phase. The manner in which macroscopic convection can give rise to dislocations through thermal stresses is illustrated by Fig. 4.

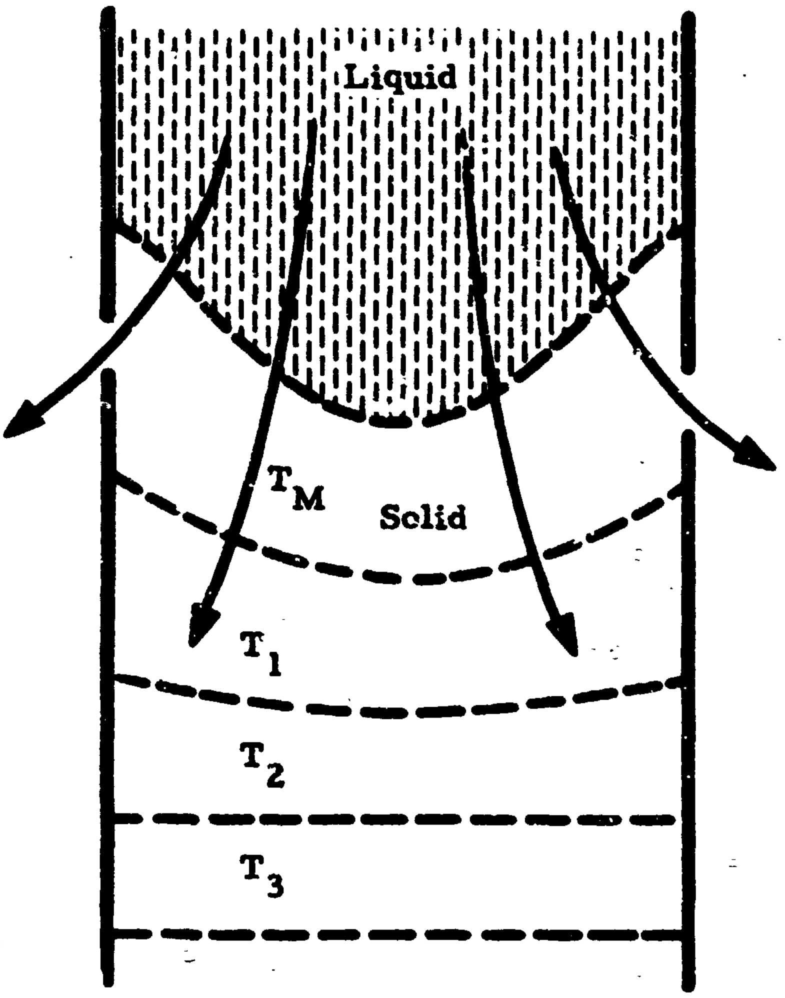


Fig. 4 - Possible Temperature Isotherms in a Crystal During Freezing (Ref. 22)

Figure 4 shows the temperature isotherms associated with a concave (to the liquid) interface shape. Near the solid-liquid interface, the temperature at the outer surface of the solid is lower than the temperature near the center. Thermal contraction, therefore, causes the outer surface to exert a compressive stress on the core of the crystal while the surface itself is in a state of tension (Ref. 22). If the solid-liquid interface is convex to the melt the inner core will be in tension and the outer in compression. When the stress σ exceeds the yield stress σ_y, plastic flow will occur which will relieve itself into dislocations. Convection can be expected to exert a significant effect on the macroscopic interface shape profiles. Figure 5 indicates the result of convection on the macroscopic interface shape during a horizontal zone melting of an organic compound.

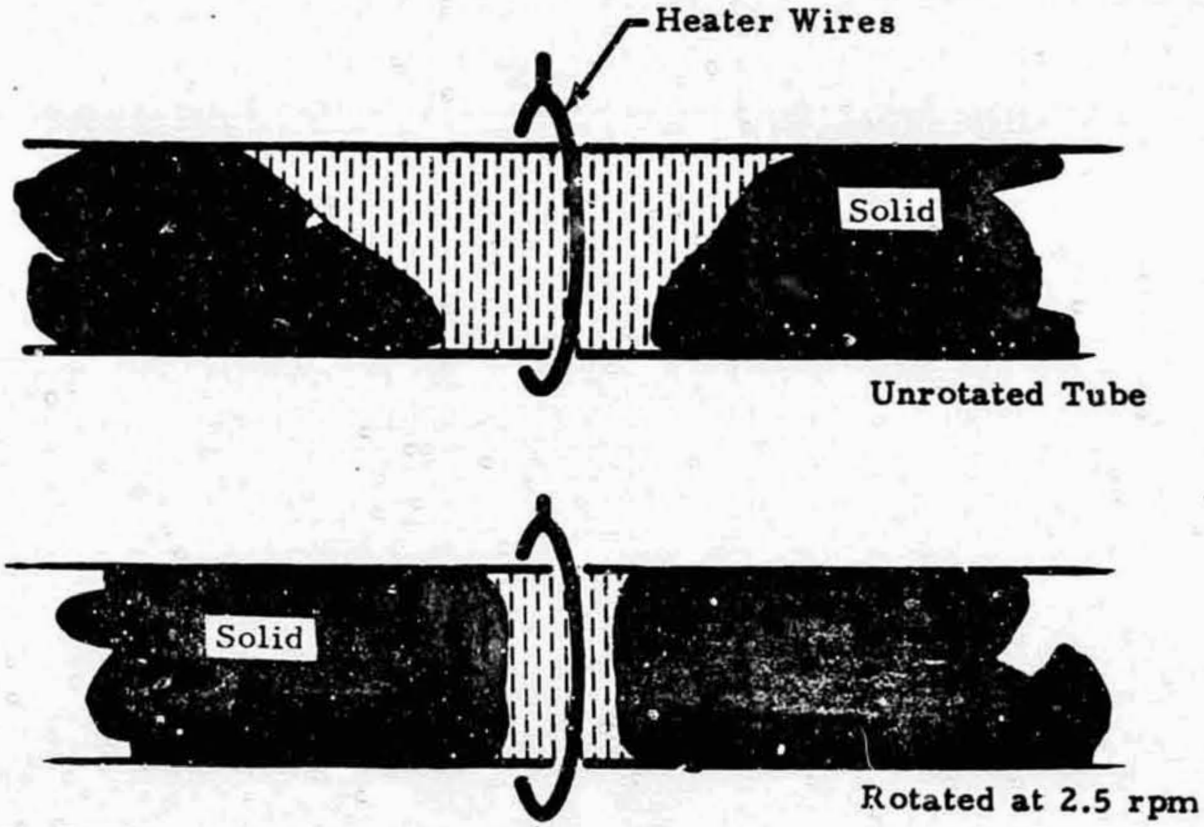


Fig. 5 - Effect of Convection on Solid-Liquid Interface Shapes in Zone-Melting (Ref. 23)

On a microscopic scale, convection is probably the cause of many puzzling crystalline imperfections. For example, temperature fluctuations having their origin in turbulent or overstable convection can result in fluctuations of crystal growth rate. Because the concentration of solute incorporated in a solid is a function of the growth rate, the result of growth rate fluctuation is a "banding" of solute in the solid (Ref. 24). Local segregation of solute on a microscopie scale can also lead to the introduction of dislocation lines at the bounding surfaces of the segregate (Ref. 25).

The appearance of the various interface morphologies as a function of the liquid temperature gradient near the solid-liquid interface is shown in Fig. 6. The morphology changes from a planar to a cellular configuration as the temperature gradient decreases and the degree of constitutional supercooling increase (Ref. 26). The appearance of the cells attributed to constitutional supercooling is quite similar to the appearance of convection cells produced in thin layers of liquids.

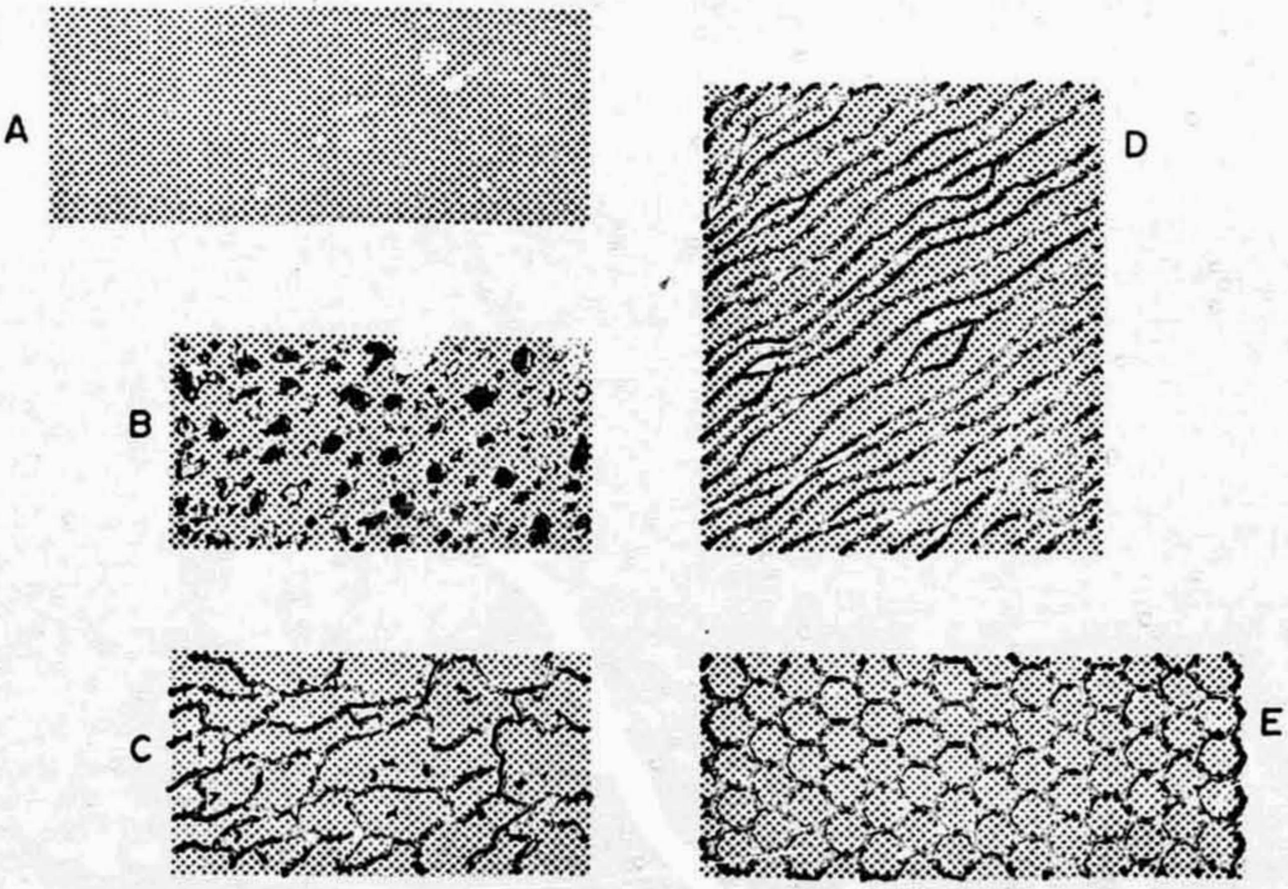


Fig. 6 - Various Morphologies as a Function of Constitutional Supercooling. Supercooling Increases from (A) to (E) (from Ref. 26)

This similarity is considered in a recent paper (Ref. 5). In this paper certain impurity patterns found in thin alkali halide crystals grown from the melt are attributed to segregation induced by microscale cellular convection.

- Mass Transfer Effects

By providing a stirring action, convection increases the rate of mass transfer to the growing crystal. On the other hand, convection by decreasing the temperature gradient ahead of a crystallizing interface increases the chance of constitutional supercooling and, thus, the likelihood of an irregular interface. Such an interface will make solvent or impurity entrainment generally more likely (Ref. 27). As the result of convective temperature or concentration fluctuations, local precipitation of impurity may result and be occluded by the growing crystal. Or, a temperature fluctuation may cause an etch pit which becomes covered over to form a minute inclusion by growing crystal (Ref. 28).

A mathematical characterization of crystal growth from a melt consisting of component A plus component B is given by the distribution coefficient. The distribution coefficient is defined as the ratio of component concentration, C_s, in the solid phase to that in the liquid, C_L. If true thermodynamic equilibrium prevailed the ratio would be k_o. During crystal growth at steady state an "effective" distribution coefficient, k, is defined by (Ref. 29):

$$k = \frac{k_o}{k_o + (1-k_o)\, e^{\left(-f\frac{\delta}{D}\right)}}$$

where f is the crystal growth velocity, δ the distance from the growing interface beyond which solute concentration is uniformly C_L. In this analysis only forced convection and inertial convection are considered. Inertial convection is the fluid flow normal to the freezing interface occasioned by volume change as the result of phase change. Cole and Winegard (Ref. 30) consider natural convection specifically. In addition to a solute boundary layer, δ_S, a thermal boundary layer, δ_T, is introduced. A thermal boundary layer is defined as the distance ahead of the interface beyond which the flow pattern becomes completely turbulent. For metals and alloys, Cole and Winegard conclude that thermal convection during horizontal solidification is of greater importance than solute convection in regard to the degree of solute macrosegregation.

In addition to the thermal and solute boundary layers, an additional boundary tape is defined in still another paper (Ref. 31). In this work a momentum boundary layer, δ_f, for metals is given by

$$\delta_S = \left(\frac{D}{\nu}\right)^{1/3} \delta_f$$

$$\delta_T = \left(\frac{K_L}{\nu}\right)^{1/2} \delta_f$$

Gravity driven convection, however, is not considered.

As yet, no comprehensive treatment of natural convection in terms of all of the various boundary layers has been found. Part of the anticipated future work will concern itself with such an elucidation.

Section 3
PRODUCT AND MATERIAL CANDIDATES FOR SPACE PROCESSING

One of two criteria must be met by any product candidate for space manufacture. These criteria are:

- The product can be made only under near zero-g conditions.
- The product can be made better or less expensive under near zero-g conditions.

In the following, five general product areas which meet one or both of these two criteria and which involve solidification as a major processing step are considered. The merits of some specific, economically valuable materials as related to possible space production are also weighed.

3.1 LARGE, PERFECT SINGLE CRYSTALS

The kinds of single crystals routinely produced for various electronic and optical applications probably number well into the thousands. The Research Materials Information Center of the Oak Ridge National Laboratory, maintains a clearing house for information on the availability, preparation, and properties of high-purity research crystal specimens. This center recently undertook to assess the demand for research crystals in the United States (Ref. 32). Questionnaires were sent to 2641 individuals in 922 different organizations. As a result of this questionnaire, a list was made of the recent most desired single crystals. The number of single crystals desired is over 60. In addition to this list of most wanted crystals the report presents some other interesting information. The estimated money spent on solid state is from 100 to 200 million, with 30 to 60 million dollars being spent annually on crystal growth. Also, some 2000 people in the United States are involved in some aspect of crystal growth. A compilation of economically valuable single crystals synthesized and characterized by the Solid State Sciences Laboratory of the Air Force Cambridge Research Laboratories is presented in Ref. 33. Another valuable review of needed crystals is given in Ref. 34.

The present study sought to identify materials whose space processing would offer not only technological benefits but also immediate economic benefits. To ascertain actual economic and production demands for specific single crystals, the present study conducted a literature survey and also a telephone survey of a number of informed sources. As a result, some 30 single crystal candidates for possible space processing were identified. A shorter list of five materials whose space production would appear to offer the most promise of economic or technological payoff is as follows

Silicon	(Si)
Germanium	(Ge)

KTN (mixture of potassium tantalate and niobate,
$K\ Ta_{1-x}Nb_x03$)
Barium Sodium Niobate (BANANAS)
Cuprous Chloride (CuCl)

Of the presented list, space processing of germanium and silicon would appear to be the easiest. The other materials have been notoriously hard to produce in acceptable single crystal form. Their economic value, however, is so great that the benefits of space processing need to be considered seriously. The case for space production of the materials presented is discussed in the following paragraphs:

- Silicon and Germanium

Although silicon and germanium single crystals are routinely grown in two-inch boules, the demand for larger more perfect crystals of these two workhorses of the semiconductor industry grows incessantly. In August 1969 an actual shortage of silicon wafers was reported (Ref. 35). The trouble apparently lies in the slicing, polishing, and layers operations. The ability to grow larger diameter silicon single crystals would result in immediate cost savings because more wafers per slice would be realized from larger diameter single crystals. Larger diameter single crystals of silicon are also in ever increasing demand for large scale integrated circuits. The cost savings in this area if larger diameter, perfect single crystals of silicon were available would be tremendous (Ref. 36).

Another attractive feature of growing silicon and germanium in space is that the growth of these two semiconductors is relatively straightforward. Both are elements and can be grown directly from the melt. Also, complex atmospheric controls are not necessary – a vacuum would work just fine.

- KTN and BANANAS

Problems of growing KTN have plagued the semiconductor industry for years. The material, in its single crystal form, is extremely valuable for modulation, switching and deflection of laser beams (Ref. 37). Single crystals of BANANAS or barium sodium nicobate have exceptional non-linear optical properties, are strongly piezoelectric, have low acoustic losses at high temperatures (Ref. 38). Because of its potentially exciting usefulness, BANANAS is presently occupying the attention and energies of a large number of investigators. With both KTN and BANANAS, convection during crystal growth appears to be the source of impurity striations which interfere with electronic or optical performance. W. R. Wilcox of the University of Southern California, a noted authority on heat transfer during crystal growth, recently expressed this opinion in regard to KTN in a telephone conversation. In the case of BANANAS growing rings are attributed to temperature fluctuations caused by turbulent-free convection (Refs. 39, 40 and 41).

The growth of these two materials is somewhat more complicated than that of silicon or germanium, apparently requiring oxygen atmosphere control. This complication, however, is relatively minor. Thus, the economic and technological payoff for large, high quality crystals of two materials make them candidates for space production.

- Cuprous Chloride

Single crystals of CuCl are electro-optical materials. Such materials find use as light modulators. The compound CuCl, however, is impossible to grow in high quality single crystal form from melt. A solid state transition occurs at 407°C; the compound has a melting temperature of 422°C. Thus, cooling a perfect crystal from melt temperature usually destroys any sizable single crystal. Solution growth, which would enable growing the low temperature phase directly, therefore, is the recommended procedure. Growth of CuCl from a KCl melt, however, resulted in optically inhomogeneous crystals (Ref. 42). An extensive analysis of the facts of CuCl grown in this manner was not undertaken, but the cellular appearance of some of the imperfections suggests that convection played an important role in their formation.

3.2 SINGLE CRYSTAL FILMS

The possibility that thin crystal films can be produced directly from melt and, more importantly, processed into a form which can be easily handled is one of the most exciting potentials of a zero-g environment. The conclusion of one analysis of the processing techniques involved in making silicon based integrated circuits is that better techniques of crystal preparation are needed (Ref. 43). In particular, it would be highly desirable to have a means of producing thin films of single crystal silicon directly from melt. At present, 50 to 75% of single silicon crystals, usually grown by the Czochralski technique, are lost in the various sawing, lapping and etching operations. Also, the number of separate tweezer-handling operations of the silicon wafers in manufacture of actual devices will far exceed one hundred. Single crystal thin films of silicon are also much in demand for solar cells. It is to be expected that thin films will have a flexibility that will make them less fragile and thus much more versatile for solar cell application – not to mention the lesser cost because of lessened handling. The foreseen advantages of a space environment for production of thin films from melt is that of lessened mechanical strain on large sheets of single crystal film. Handling problems would thus be lessened and more versatile processing procedures could be evolved.

3.3 SPHERES AND TUBES (SOLID AND HOLLOW)

Ball bearings of unprecedented tolerances is one of the proposed candidates for space manufacture (Ref. 44). The only real considerations regarding the manufacture of solid bearings is near zero-g environments are material handling problems, i.e., how to eject a quantity of molten metal so that it will remain levitated long enough to assume a near perfect spherical shape; how to cool the molten levitated sphere under zero-g; how to collect the solidified spheres; etc. This assurance as to the feasibility of manufacturing solid ball bearings is possible because near zero-g environments via free fall are routinely used on earth for the same purpose, e.g., lead shot. Also, very small spherical single crystals of alloys have been made by solidifying alloy melts in very small ceramic tubes (Ref. 45). One consideration which may be of importance with some metals is that of anisotropic crystal growth rates. Growth rate anisotropy is not expected to be a problem as long as a large number of nucleation sites exist, thus assuring a fine grained product. Conceivably where crystallization proceeds from only one nucleation site, the molten sphere might possibly crystallize into a geometrical shape. Such a rather unlikely possibility is amusingly illustrated in the following photograph. The photograph is an altered version of Sir John Everette Mellais' painting "Bubbles." Dr. G. A. Chadwick of Cambridge University supplied the negative.

Fig. 7 - Zero-G Phenomena May be Surprising

Dr. Chadwick actually used the photograph to illustrate anisotropic solid surface tensions. Small bubbles observed in ionic solids have a decided crystallographic appearance (Ref. 46). These polyhedral "holds" are attributed to extreme anisotrophy of the solid surface energy even at temperatures approaching the melting point. Liquids, however, generally do not exhibit surface tension anisotropy.

In the case of liquid crystals, however, anistropic surface tension does result in non-spherical liquid equilibrium shapes (Ref. 47). Figure 8, reproduced from Ref. 47, shows some of the equilibrium shapes postulated. Tactoids, Fig. 8b, apparently have been observed in colloidal solutions and in some plant virus preparations.

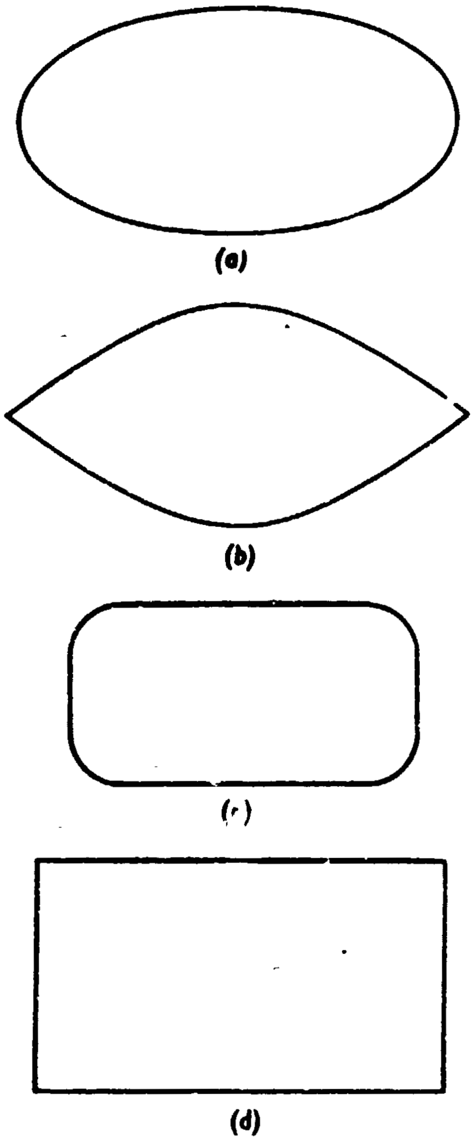


Fig. 8 - Equilibrium Shapes of Liquid Crystalline Drops (Ref. 47)

The influence of solid surface tension is important only on a microscopic scale. The forces involved are much too small for any sizable mass transfer (Ref. 48). The possibility of crystallizing liquid crystals directly into unique shapes, however, is an interesting note.

Unlikely as the possibility of directly solidified cubes, etc., at present appears, possible ramifications of growth rate and solid surface tension anisotropy should be considered further. For one thing, directly solidified single crystal geometrical shapes or solid foams with square bubbles may be highly profitable products. Such polyhedrons would indeed represent unique products.

The elucidation of the advantages of a zero-g environment in producing hollow ball bearings awaits further advancement in the state of the art of materials. First of all some stabilizing agent for molten metal films will have to be defined. Stable bubbles of most pure materials are not possible without the presence of an additive. Some additive, analogies to soap in water, will have to be found for metals before the concept of producing hollow ball bearings can be regarded as feasible. Once such an additive has been found then other secondary problems such as the volume change which occurs on crystallization, the number of nucleation cites, convection, etc. In regard to stable bubble formation, it would be interesting to experiment with chemical compounds like or similar to saponon. Saponin does form stable bubbles which apparently can be solidified directly (Ref. 49).

Finally, the foreseen advantages of zero-g to grow hollow tubular crystals is that of lessened mechanical strain in the produced tubes. This lessened mechanical strain would allow longer, straighter tube to be grown directly from melt. Two reports of such tubes have been found in the literature. Single, bi-, and tri-crystalline tubes of ice were grown directly from water over which a vacuum was maintained (Ref. 50). Also, tubes of germanium have been grown by Russian investigators (Ref. 51). Uses for such tubes is at present unknown. The recent use of thin films for wave guides for acoustic signals (Ref. 52), however, suggests that a use for hollow, crystalline tubes would soon be found.

3.4 DIRECTIONALLY SOLIDIFIED COMPOSITES

A number of unusual and unique products as the result of undirectional solidification of multi-component melts have been suggested. These include metal alloys, magnetroresistive and infrared polarizing materials, supercooling materials, and optical materials (Ref. 53). Nickel, cobalt, columbium, and tantalum alloys which are stronger than any commercial alloys of the same base metal have already been produced by this method (Ref. 54).

In one study of the morphology generated by undirectional solidification of eutecties, a classification of the structure as a function of the degree of constitutional supercooling is given (Ref. 55). The table given in the reference is reproduced as follows:

Table 1

SOLIDIFICATION STRUCTURE AS A FUNCTION OF CONSTITUTIONAL SUPERCOOLING

	Degree of Constitutional Undercooling				
Single-phase alloy	Planar	Two-dimension Cells	Three-dimension Cells	Dendrites	Equiaxed
Eutectic alloy		Lamellar	Rods or Broken Lamellar	Dendritic or crystallo-graphic	Acicular Globular

The degree of constitutional supercooling ahead of a single-phase planar interface is a function of (1-ko)/ko, R, and G_L where k_o is the equilibrium distribution coefficient, R the rate of growth, and G_L the temperature gradient in the liquid. For eutectic solidification, a eutectic distribution coefficient, k_e, is defined as the ratio of the solubility in the solid divided by the solubility in the liquid. Ahead of each solid phase in a solidifying eutectic a different k will obtain. The structure of the eutectic will depend primarily on the values of $(1-k_e)/k_e$, R, and G_L ahead of each solid phase. As observed previously, a steep, positive temperature gradient ahead of a solidifying interface tends to supress constitutional supercooling. A steep temperature gradient, however, also tends to increase the likelihood of convection which has the effect of lessening the temperature gradient. It can thus be appreciated that convection can have a profound influence on the microstructure of directionally solidified composites. The role of convection in a number of directionally solidified eutectic experiments has been considered briefly (Refs. 56, 57 and 58). Much, however, remains to be done in this area.

3.5 POSTULATED UNIQUE PRODUCTS

Other unique products based on solidification processes can be postulated. For example, by controlling the freezing rate it should be possible to solidify a monotectic so that the solid forms a uniform fibrous dispersion. A monotectic is a multicomponent melt (liquid 1) which "freezes" to a solid and another liquid (liquid 2), i.e., liquid 1 $\rightleftarrows$ solid + liquid 2. Liquid 2 can then be blown out leaving a fine porous matrix (Ref. 59).

A composite material consisting of inverse bubbles of one phase within another phase should certainly possess unique properties. An inverse bubble is a spherical film of one material within another material. In the case of air bubbles in a liquid, an inverse bubble has the following configuration (Ref. 60).

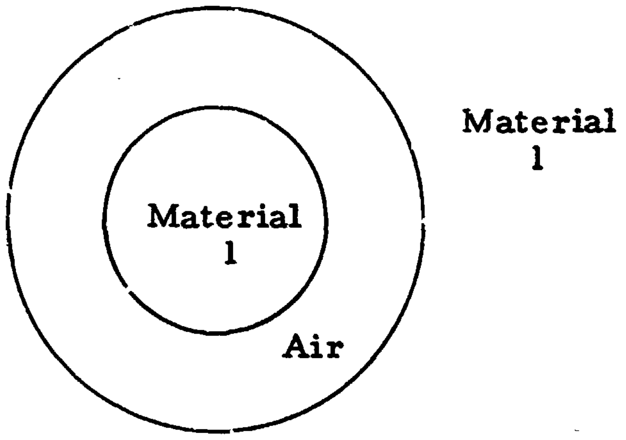


Fig. 9 - Structure of Inverse Bubbles

If it were possible to obtain such bubbles with materials which could be solidified with the bubbles intact, a truly unique product would be produced. The advantage of zero-g environment for the production of such a product would be dispersion stability during solidification. The two products just mentioned are, of course, highly speculative at present. More investigation is indicated.

Section 4
PROCESSING CONCEPTS

4.1 MELT GROWTH OF LARGE SINGLE CRYSTALS

Melt growth is presently the most frequently used technique for production of semiconductor single crystals. The Czochralski method is the common technique used. The salient features of the Czochralski techniques are shown in Fig. 10.

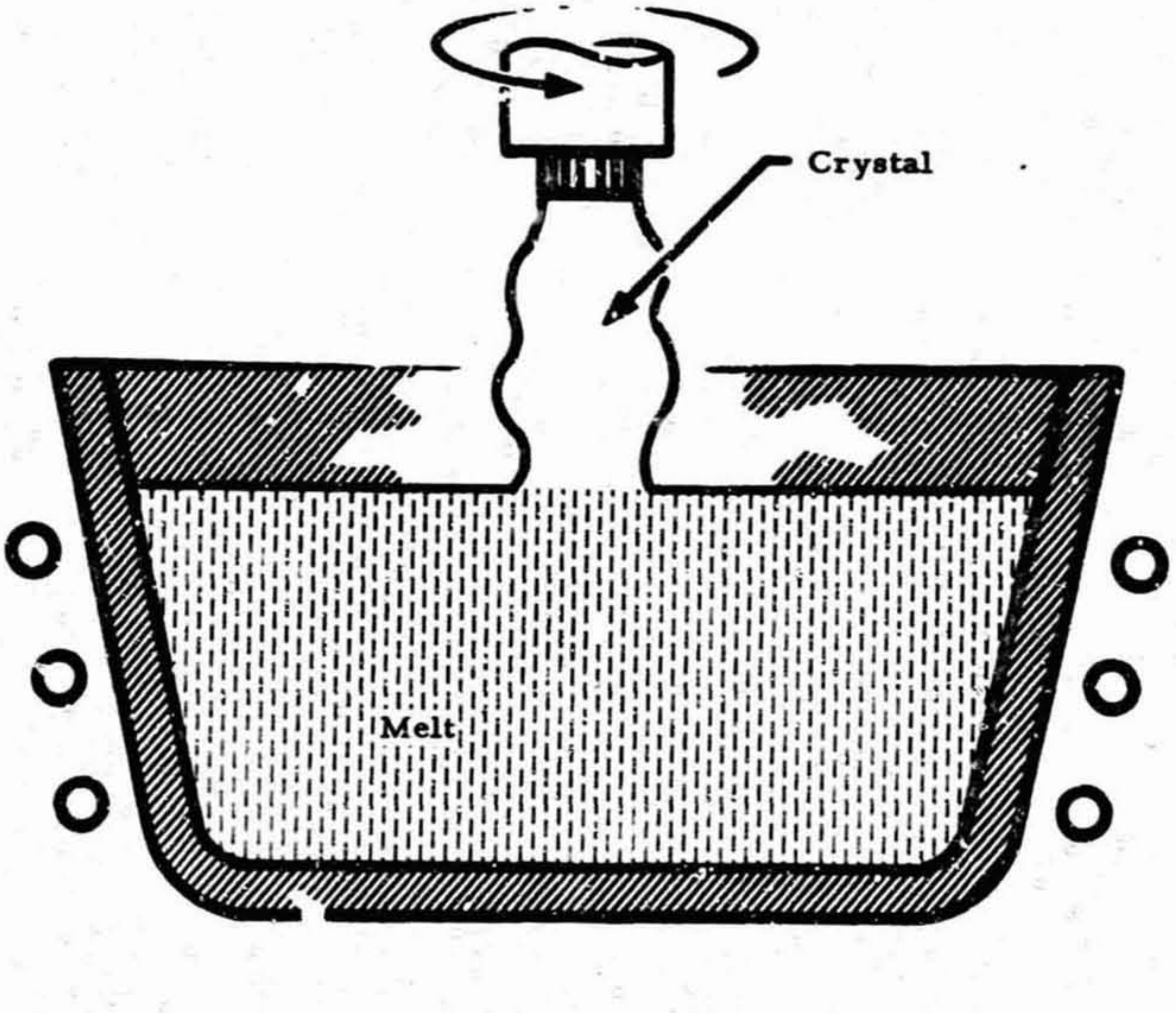


Fig. 10 - Czochralski Crystal-Growing Arrangement

Material melt is contained in a heated crucible. A seed crystal is brought into contact with the melt surface. After wetting is completed, the seed is slowly withdrawn. The diameter of the pulled crystal is controlled by controlling the temperature of the melt and the rate of crystal pulling. Also, the crystal is rotated as it is withdrawn to eliminate thermal asymmetry. The melt may also be rotated for greater control of the thermal conditions.

One of the great advantages of the Czochralski method is that controlled amounts of impurity can be readily added to the melt. Proven as the technique is under earth conditions, it does not appear to have a very high potential for operation in a zero-g environment without drastic modification. For one thing, some sort of restraint must be put on the melt. A completely containerized melt with the crystal pulling occuring through a slot is conceivable. Many foreseen problems, however, can be anticipated with such an arrangement, introduction of additional thermal gradients to name one. Restraint of the melt by magnetic means is another possibility in some cases, but probably too complicated in actual practice. A more likely possibility is the pedestal method which is a combination of the floating-zone and Czochralski techniques. This technique will be discussed subsequently.

The floating-zone method appears to be directly adaptable to a near zero-g environment. No real objections to operation in space environment can be raised.

The salient features of the floating-zone technique are illustrated in Fig. 11. A molten band or zone is produced in a rod of polycrystalline material. The method of heating may be radiant, induction, or electron-beam bombardment, depending upon the physical characteristics of the particular material being processed. The molten zone is caused to pass along the rod, by moving the heat source, with melting occuring at one interface and freezing at the other. By introducing a properly oriented seed at the freezing interface and controlling the rate of zone travel, single crystal growth can be accomplished. The main advantage of the technique is that crucible-melt contact is avoided thereby eliminating a potential source of contamination. Under 1-g condition, however, the size of the molten zone is limited by the need for surface tension to balance the hydrostatic pressure of the liquid. Also, a limiting factor is the tendency of surface tension to reduce the liquid surface area. A long thin molten zone would show a tendency to separate.

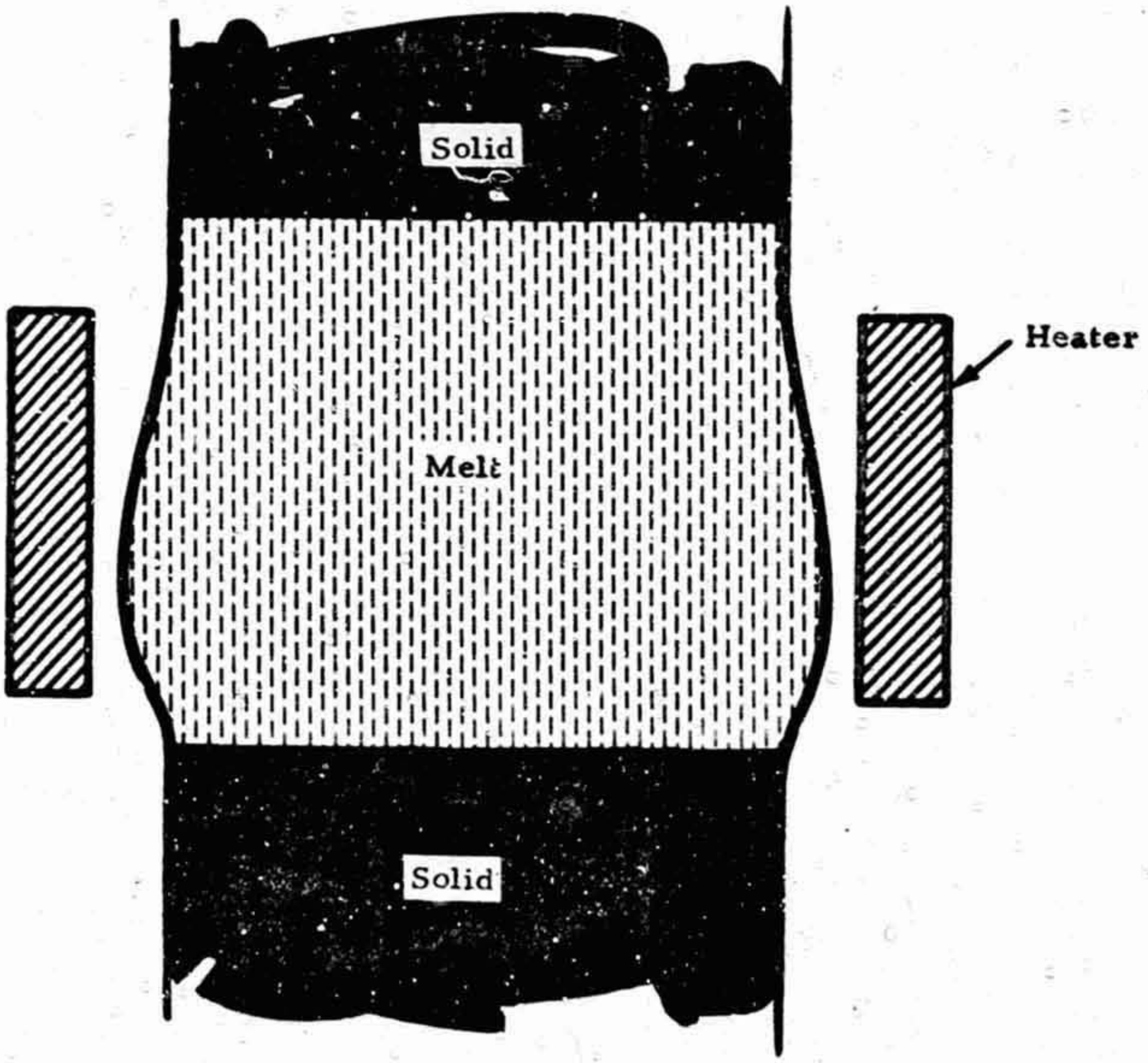


Fig. 11 - Salient Features of a Floating-Zone Crystal Growing Arrangement

Even further improvement of crystal quality and crystal size might be realizable for some materials under zero-g with the pedestal method. A schematic of the apparatus is shown in Fig. 12. (Ref. 61)

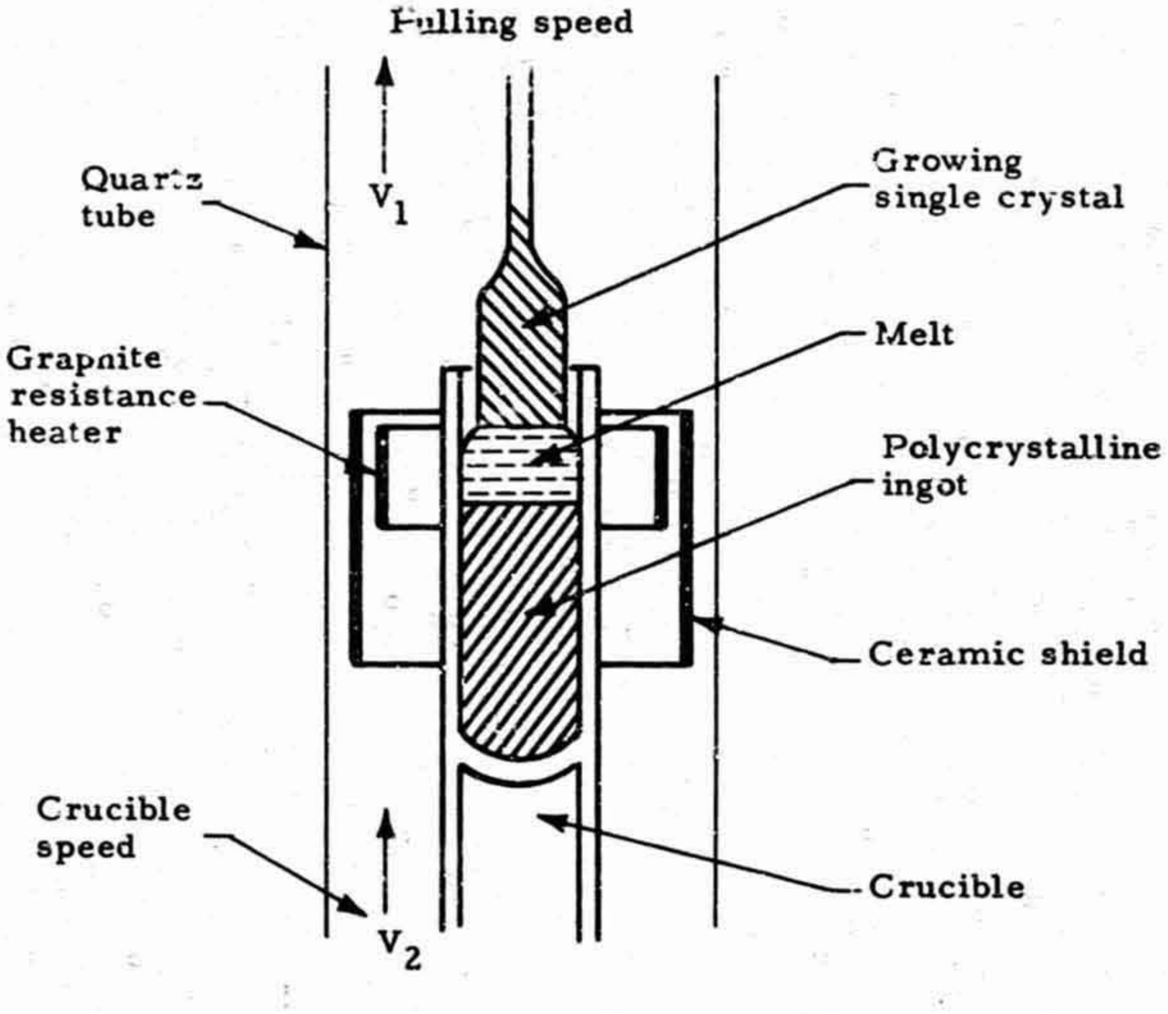


Fig. 12 - Schematic of Pedestal Apparatus (Ref. 61)

The definition of the molten zone and crystal shape with no gravity restraining force will be an interesting analytical problem.

Because of atmosphere or decomposition problems, it may be advisable in some instances to utilize contained crystal growth. In many cases the well-known Bridgman technique or Stockbarger method will probably be the most suitable. The essentials of this method are illustrated in Fig. 13.

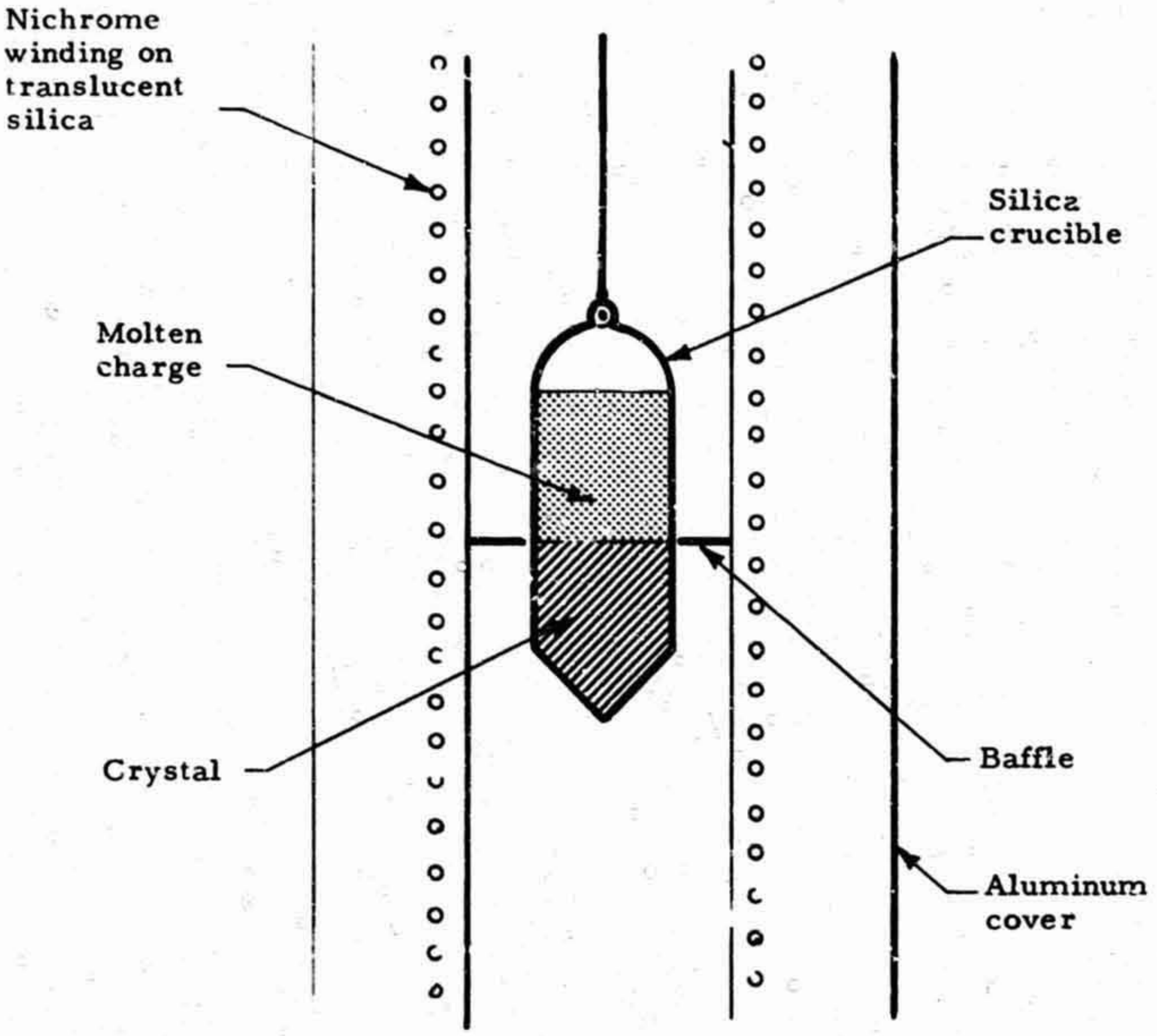


Fig. 13 - The Bridgman Technique (Ref. 62)

In this method molten material in a crucible is lowered from a hot furnace into a cooler one. Growth begins when the pointed tip cools below the melting point of the crystal. Operation of this technique in zero-g would require that the melt wet the crucible.

4.2 SOLUTION CRYSTAL GROWTH

Solution growth offers the advantage of crystal growth at a lower temperature than would be possible in melt growth. An exhaustive theoretical analysis of the role of gravity convection in solution growth was recently reported by one of the foremost recognized authorities on crystal growth, W. A. Tiller of Stanford (Ref. 63). As the result of this analysis, Tiller proposes the arrangement shown in Fig. 14 for long term stability and programmed crystal growth.

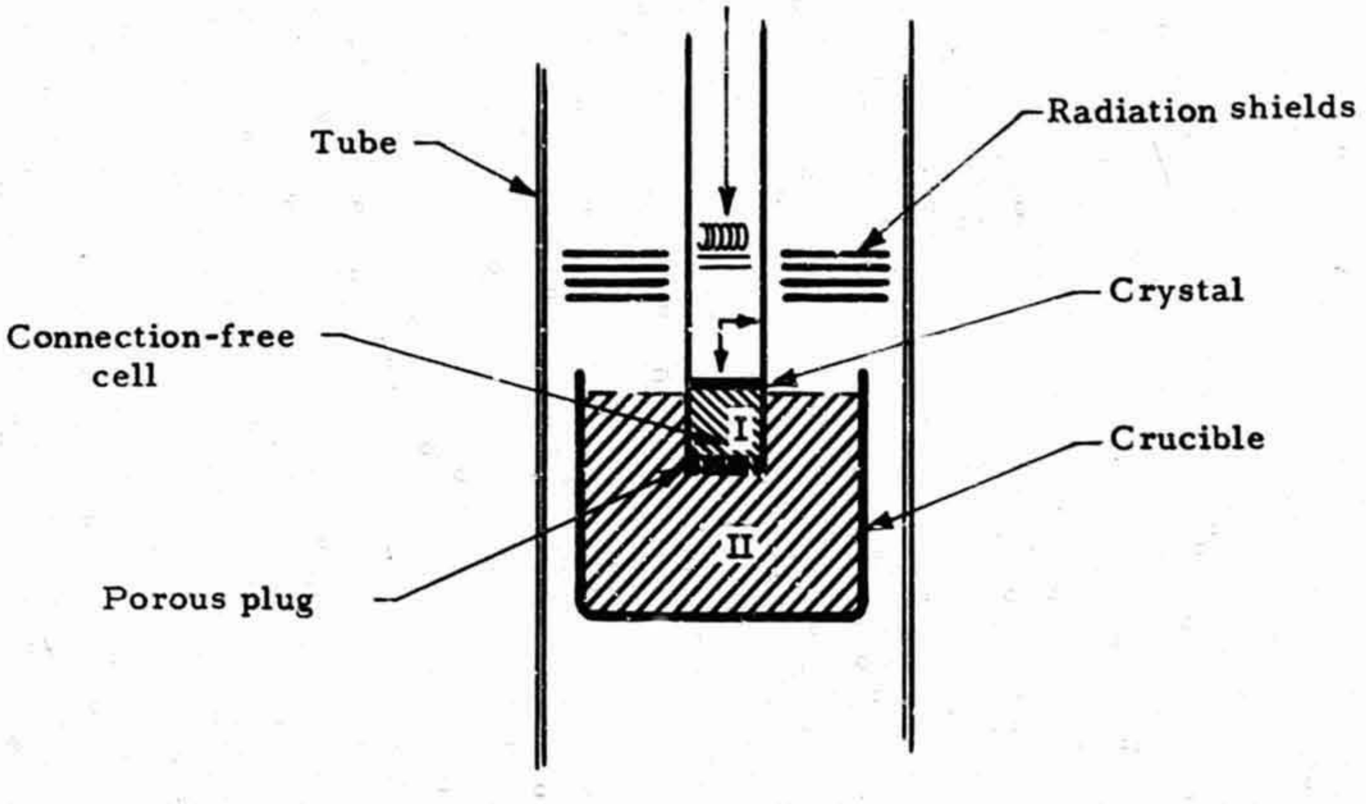


Fig. 14 - Schematic of Tiller's Proposed Cell for Solution Growth (Ref. 63)

In region II the bulk liquid is completely mixed by forced convection, while region I is completely convection free. The porous plug prevents convection flow from region II to region I. The radiation shield is a further precaution against severe temperature gradient leading to convection.

Component concentration in the region II is maintained by a vapor feed procedure.

For growth at near zero-g a number of modifications can be proposed. The melt will have to be completely contained. Control of the solute concentration can be accomplished either by vapor feed, slow solution, or mechanical addition. Which procedure would be advisable awaits future analysis.

It should be noted that even though forced convection is required in region II even under zero-g with this arrangement, the elimination of <u>all</u> convection in region I would result in a much superior product.

Other arrangements based on solution crystal growth can be devised for zero-g operation. One of these is the "temperature gradient zone melting" (TGZM) technique described by Pfann (Ref. 64). In this technique, a thin layer of solid solute is sandwiched between blocks of solid solvent. The whole arrangement is then placed in a stationary temperature gradient. A molten zone will result because a solution will have a lower melting point than a pure solvent. Because of the action of the various rate processes -- solution, diffusion, and freezing -- the molten zone will migrate through the block. Figure 15 illustrates the physical situation

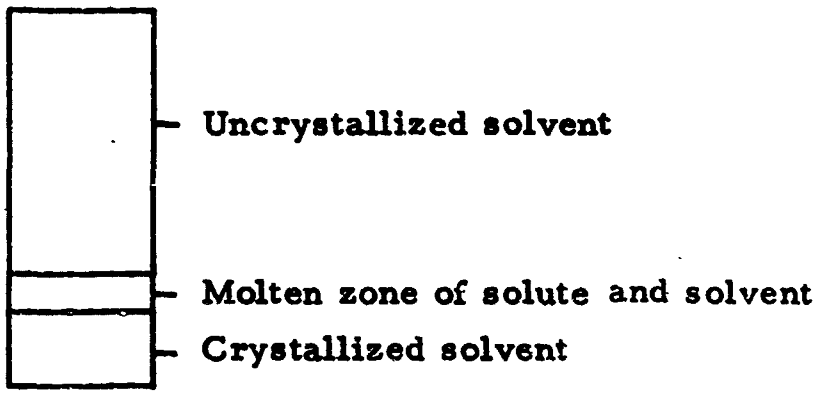


Fig. 15 - Schematic of Temperature Gradient Zone Melting

An analysis of the technique and several variations are discussed in some detail in Ref. 65. For the production of semiconductor single crystals the technique appears quite promising. A number of specific studies including those on GaAs, α-SiC, and GaAs/GaP heterojunctions, have already been conducted (Ref. 65). One of the most important advantages of the technique is the dramatic reduction of constitutional supercooling. Presumably operation of the technique in zero-g would further enhance the reduction. Probably other advantages such as large molten zones would also obtain in near zero-g.

Finally, in some cases the technique of allowing a freely suspended crystal to grow from solution may offer advantages in zero-g. In one-g, it has been found that curves of equal concentration as observed by an interference microscope are deformed (Ref. 66). Increased convection at various paces caused crystal growth to be accelerated. Apparently, zones where increased convection was observed correlated with resultant solution inclusions.

Section 5

MATHEMATICAL FORMULATIONS OF CRYSTAL GROWTH

A great variety of factors involved in crystal growth have been discussed in previous sections. Many others have not even been touched on. Reference 1 considers some other aspects of crystal growth at greater length. Obviously, any mathematical analysis must severely limit the area of interest and applicability. For the purposes of evaluating as yet unknown space processing concepts, however, it is desirable to have general criteria for deciding which physical processes are predominant. Such criteria definition is projected work for the near future. Much of the groundwork for such criteria definition has been laid in the course of the present, reported study.

Projected future studies are seen as delineating the mathematics of the whole range of known physical phenomena involved in crystal growth. Once this delineation is completed, criteria for application will be defined. With the aid of these criteria it should then be possible to simplify the mathematics so as to make them amenable to either computer or analytical solution.

The following simple example pursued for a short time in the present study will illustrate the approach. Probably the crystal growing technique which will be most used in near zero-g environments will be the floating-zone. With this technique, it will be highly desirable to have a means to predict how the shape of the freezing interface is influenced by the rate of molten zone travel. The physical situation at study state is as shown in Fig. 16.

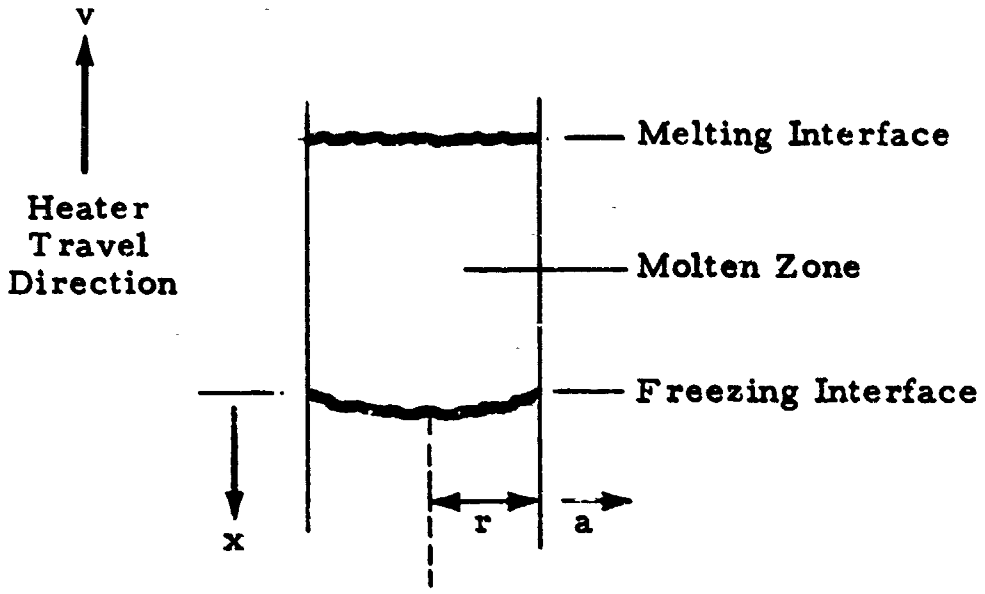


Fig. 16 - Mathematical Model of Zone Melting

The temperature distribution within the cylindrical rod satisfies the differential equation (Ref. 67).

$$\frac{\partial T}{\partial x} + \frac{\partial T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} - 2p\frac{\partial T}{\partial x} = 0 \qquad (1)$$

where

$$p = \frac{v}{2K}$$

where K is the thermal diffusivity.

Obviously, depending on the ratio of the velocity of crystallization and the thermal diffusivity, the p term may or may not be important. If it were unimportant, its neglect would probably simplify the solution of equation 1 considerably.

Other considerations such as steady-state temperature distributions along the solidifying rod and the mathematical description of surface tensions driven flows were also examined in the present study. It may be of interest to indicate here some of the considerations obtaining in surface tension flows.

As I discussed in the Appendix, if a surface is curved the only discontinuity is in the hydrostatic pressure in a direction normal to the surface. This discontinuity for a liquid sphere is given by the well known equation

$$P_E - P_T = \frac{2\gamma}{r}$$

where P_E and P_T are the external and internal hydrostatic pressures, and r the radius of the curvature. The term $\frac{2\gamma}{r}$ is called a surface pressure, π, by some authors. If the surface tension varies along the surface because of temperature or concentration variations, a tangential stress variation is set up.

Between two phases, therefore, a discontinuity in the bulk tangential stress is set up proportioned to the variation of surface tension gradient or surface pressure gradient. More completely, the shear stresses exerted by the bulk phases is given by Ref. 4c.

$$\begin{array}{lclcl}\text{Shear stresses} & & \text{Surface pressure} & & \text{Surface} \\ \text{exerted by} & = & \text{gradient} & + & \text{dilational} \\ \text{bulk fluid} & & & & \text{stress} \\ & & & & \\ & & + & \text{Surface} & \\ & & & \text{shear stress} & \end{array}$$

Simplification of the preceding equation to easily produce accurate physical and mathematical approximations of floating-zone crystallization is the subject of projected future studies.

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Appendix

MECHANICAL AND THERMODYNAMIC EXPLANATIONS OF SURFACE TENSIONS

Appendix

MECHANICAL TREATMENTS

Mechanical treatments of surface tension presented in the literature tend to be confusing. A bothersome point frequently encountered is how the liquid surface can be in a state of tension when a liquid is defined as material that cannot withstand a shear stress. The confusion regarding this point appears to stem from a failure to clearly define pressure terms. For example, the following list of pressure terms are encountered in the literature on surface tension:

Hydrostatic pressure
Thermodynamic pressure
Total pressure
Cohesive pressure
Intrinsic pressure
Internal pressure
Molecular pressure
External pressure
Applied pressure
Thermal pressure
Kinetic pressure
Capillary pressure
Surface pressure.

It is probably well, therefore, to reconsider the concept of pressure and the manner in which it may be possible to clarify the various pressures giving rise to surface tension. The following discussion, while possibly not rigorously precise concerning subtle nuances of pressure regarded as a tensor term, present a fairly simple visual concept of surface tension forces and their operation. The discussion follows the presentation of Brown (Ref. 68) for the most part. Several original modifications, however, have been incorporated into Brown's treatment.

Consider a rather sizable, free floating liquid drop as in zero-g. Two pressures, acting in the same direction, keep the drop intact. These two pressures are a cohesive, internal, or intrinsic pressure, P_o, and an applied external pressure, P_E. Acting in opposition to these two pressures is a thermal pressure, P_T. The thermal pressure arises from the thermal motion of the molecules. The thermal pressure, or the total pressure as some call it, is the pressure that is independent of direction within a liquid. The cohesive pressure P_o has its origin in powerful short-ranged attractive forces. In the interior of the liquid these attractive forces acting on any given volume element are all of the same magnitude regardless of direction and so cancel out. Near the liquid surface, however, the surface molecules experience an unbalanced attraction - more toward the liquid and less toward the vapor.

The cohesive pressure, in other words, is not the same in directions normal and parallel to the surface. At equilibrium, the following equations may be written:

Normal to the surface

$$P_T = P_o + P_E$$

Parallel to the surface

$$\sigma_T = \sigma_o + \sigma_E$$

Pressures parallel to the surface are written here as stresses only to distinguish clearly the different directions.

Right at the dividing surface we may say that P_o is essentially zero because the attractive forces of vapor molecules for liquid molecules and vice versa are quite small. This decreased attraction in a normal direction to the surface is puzzling at first encounter. Brown, however, gives a neat explanation (Ref. 68, p. 431). The surface may be viewed not as static but in a state of dynamic equilibrium. Because the surface molecules possess higher potential energy than the rest of the liquid, their density is less than in the rest of the liquid. As a result the pressure at the surface is less than in the rest of the liquid. In other words, "the potential energy which a molecule would lose by moving from the surface into the interior is equal to the potential energy of strain which the surface layer would gain by this transfer." As we descend into the liquid P_o increases. Because P_T is equal to σ_T, we may write

$$P_o + P_E = \sigma_o + \sigma_E$$

and since in the surface layers

$$\sigma_o > P_o$$

then

$$\sigma_E < P_E,$$

which implies a state of tension parallel to the surface. The surface tension, however, is defined as the force per unit length required to extend a film a certain distance and is given by

$$\gamma = (P_E - \sigma_E)t$$

where t is the thickness of the surface layer. The actual tension in the surface layer is given by $-\sigma_E t$.

CURVED SURFACES

The following illustrations show three possible curvatures of liquid/gas interfaces.

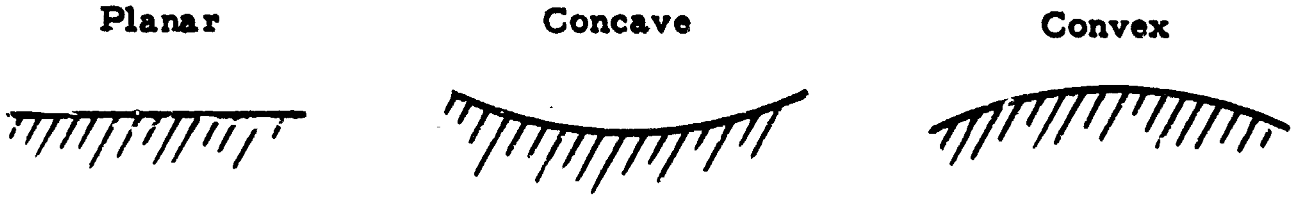

Fig. 17 - Possible Liquid Surface Curvatures

Assuming that the liquid surface is in a state of tension, it follows that the pressures on either side of the interface are equal for a planar interface or unequal for curved interfaces. The question is how the various pressures are altered by a curved interface. As discussed previously, right at the boundary between liquid and vapor, P_o is essentially zero. For a planar interface, therefore, $P_T = P_E$. In a liquid whose surface is concave to the vapor, the liquid above a small volume element in the surface exerts an attractive force on the element. The situation may be represented as shown in the following diagram (Ref. 49, p.8):

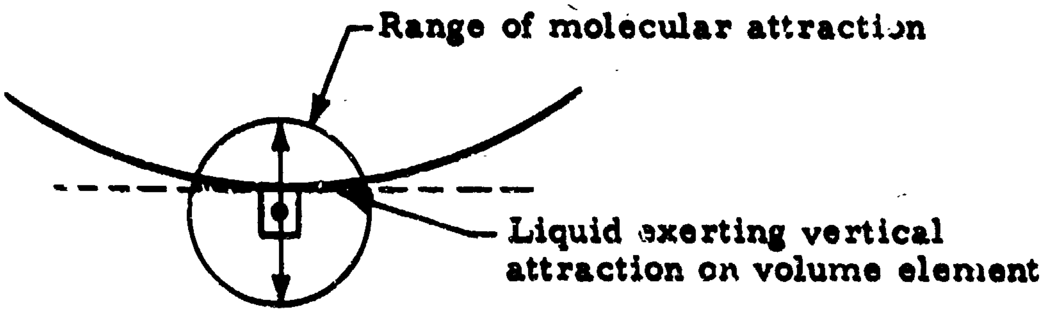

Fig. 18 - Attraction on Small Volume Element in Concave Liquid Surface

In this case P_o is not zero right at the surface, but adds to the thermal pressure, i.e.,

$$P_T + P_o = P_E$$

In a liquid surface concave to the vapor P_o is subtracted from P_T, i.e.,

$$P_T - P_o = P_E$$

So that in a concave liquid surface P_E is greater than P_T, and in a convex liquid surface, P_T is greater than P_E. The pressures σ_E in the direction of the surface are correspondingly increased or decreased because of the equality $P_T = \sigma_T$. If the σ_o terms are unaffected by surface curvature the surface tension given previously by

$$(P_E - \sigma_E)t$$

is also unaffected by surface curvature. This result is in accord with the literature (Ref. 69, p. 138). Presumably for extremely small drops where the curvature is extreme the σ_o terms would be affected, and so the surface tension would also be affected.

THERMODYNAMIC FORMULATIONS

Perhaps because of the confusion regarding the manner in which a surface tension might arise, a number of authors would deny the existence of surface tension altogether. Surface tension in these treatments is regarded as a convenient fiction with surface energy as the ultimate reality. While not sharing this view, the present study recognizes the additional insight value of the thermodynamic approach and so presents a brief outline of its salient features.

A surface energy is defined as the work required to move a molecule from the interior of a liquid to the surface. The energy change involved in extending a liquid fil from a state of zero surface area to a state of surface area A, ignoring volume effects, is given by

$$\Delta E = q - \gamma A$$

The heat term q is given by λA where λ is further defined as a heat supplied at constant temperature per unit increase of area. By performing an analysis of a cycle in which the surface is increased and decreased at constant temperature, and the temperature raised and lowered at constant area, the latent heat of surface extension is found to be (Ref. 69)

$$\lambda = -T\left(\frac{d\gamma}{dT}\right)$$

The increase in energy of the film per unit increase in area is, therefore,

$$\Delta E_a = \gamma - T\frac{d\gamma}{dT}$$

In the preceding equation ΔE_a can be identified with the total surface energy and γ the free or available surface energy.